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Project Summary

Low Ozone-Depleting Halocarbons As Total-Flood Agents: Volume 2—Laboratory-Scale Fire Suppression and Explosion Prevention Testing

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Adequate protection of enclosed facilities against explosions and fires involving flammable gases or streaming liquid fuels poses a major safety challenge for the Alaskan North Slope petroleum industry. At present, such facilities are protected by Halon 1301 total-flood systems. However, because of its depletion of stratospheric ozone, the production of Halon 1301 was halted under international treaty on December 31, 1993. The report gives results from flame suppression testing of potential Halon 1301 replacement chemicals in a cup burner using *n*-heptane fuel and inertion testing in a small-scale explosion sphere, with propane and methane as test fuels. Test equipment and techniques are described. Fire suppression test results are given for a wide range of halocarbon chemicals. For inertion testing, differences between Halon 1301 inerting concentrations, determined using the current test apparatus and previous testing, are briefly discussed. Agent performance is given in terms of the concentration required to achieve flame extinguishment or inertion, defined as an explosive overpressure of 1 psi (6.9 kPa) or less, and weight and storage volume equivalents, reflecting the weight and storage volume of a replacement agent required to achieve the same effectiveness performance as Halon 1301.

This Project Summary was developed by EPA's National Risk Assessment Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Enclosed spaces containing flammable hydrocarbon fuels present challenging fire and explosion protection problems. Of particular concern are Alaskan North Slope petroleum handling facilities, where leaks of flammable gaseous and liquid hydrocarbons can occur, presenting both fire and explosion hazards. At present, the primary fire and explosion protection measure for such facilities is total-flood application of Halon 1301. However, due to depletion of stratospheric ozone, the production of halon fire extinguishing agents (including Halon 1301) was banned as a result of an international treaty, the Montreal Protocol. The report describes the laboratory-scale experimental evaluation of a number of halocarbon candidates as Halon 1301 replacements for total-flood application in enclosed facilities such as those found at the Alaskan North Slope.

Two types of halocarbon chemicals were emphasized in this effort: (1) physical action agents (PAAs), which extinguish flames by physical means such as heat absorption, evaporative cooling, thermal dissociation, and separation and dilution of fuel and oxygen, and (2) chemical action agents (CAAs), which cause fire suppression primarily by free radicals catalytically interrupting the combustion chain reaction mechanism. CAAs generally are more effective at suppressing fires and explosions than PAAs. The designation of chemicals into these categories does not imply that agents operate exclusively by one mechanism or the other, rather that one action appears to be the predominant mode of extinguishment.

A list of PAAs and CAAs was developed in a previous effort. Candidates were separated into categories based on availability and toxicity information. Those chemicals that are available in bulk now or apt to be in the near future and which have a significant amount of toxicological information known indicating that they are low in toxicity are given highest priority for testing. The results of testing these chemicals are presented here.

Fire Suppression Testing

Fire suppression effectiveness of 71 halocarbon chemicals was determined in the laboratory cup-burner apparatus using *n*-heptane as the fuel. A reduced-scale version of the widely known Hirst and Booth cup burner was used. Extinguishment values are calculated from molar flow rates for gases or volumetric flow rates for liquids and reported as volume percent concentration. The weight and storage volume equivalents are calculated relative to Halon 1301 in order to compare fire suppression performance to the reference agent. Results of the cup burner testing are presented in Table 1.

Explosion Prevention Testing

Explosion prevention or inertion testing was performed on 34 chemicals in an explosion sphere modeled after the Fenwal Safety Systems explosive sphere. The apparatus consisted of two 25-cm diameter stainless steel hemispheres hinged together to contain a volume of 7930 cm^3. A stoichiometric mixture of fuel (propane or methane), air, and inerting chemicals was introduced into the sphere using the partial pressure method. The mixture was ignited by a variable-power direct-current (dc) spark generated between two electrodes in the center of the sphere. The resulting overpressure was measured. The volume percent concentration at which the overpressure did not rise above 1 psi (6.9 kPa) was considered the inertion concentration for stoichiometric fuel and air mixtures (IC_{st}). Weight and storage volume equivalents were calculated using Halon 1301 as the reference chemical. The results of the inertion testing are presented in Table 2. Limited testing to determine the flammability diagrams or envelopes indicates that higher concentrations may be required to inert non-stoichiometric fuel and air mixtures. Therefore, testing at other than stoichiometric fuel-to-air ratios should be undertaken before setting design specifications for a particular agent.

Conclusions

Results obtained from this study represent laboratory-scale testing within controlled parameters. Methods employed in this effort proved to be reliable and repeatable for agent screening and ranking a number of halocarbons. However, care must be taken not to extrapolate these results to larger scale without verification. Results of the fire suppression and explosion prevention testing clearly demonstrated that those agents containing either bromine or iodine exhibited superior effectiveness. However, several considerations must be taken into account when recommending which chemicals should be investigated further as candidates for replacing Halon 1301. Since this effort emphasized protection of North Slope oil and gas facilities, the nature of the threat unique to these applications was of key importance. For the most part, the North Slope facilities are generally accessible to humans, although some areas are occupied only intermittently or infrequently. Because human occupancy is a major concern, the toxicity of the candidates must be sufficiently low to allow for human exposure at safe levels.

With the production phaseout of new Halon 1301 at the end of 1993, the North Slope facilities will need to continue their fire and explosion protection measures using either Halon 1301 or other chemicals or technologies. To the extent that insufficient supplies of recycled Halon 1301 are available for North Slope use in the near-term, replacement agents will be needed. The need for a near-term replacement limits the number of chemicals that can be considered as candidates to only those which are available now or will be available in the near future. Also, a significant amount of toxicity information must be known about a chemical to allow its use in occupied areas. Additionally, a number of federal and state regulatory approvals must be obtained before new agents can be used.

At the time of this project, the National Fire Protection Association (NFPA) had selected a number of Halon-1301 replacement candidates with potential for use in the near-term. Those candidates selected by the NFPA are shown in Table 3. All of these chemicals, including HCFC Blend A, were evaluated at laboratory scale by this study. The extinguishment and inertion concentrations for HCFC Blend A were found to be no different than for the major component, HCFC-22, and therefore results of this blend are not reported separately in Tables 1 and 2. The candidates in Table 3 did not exhibit the best performance for fire suppression or explosion prevention effectiveness in this laboratory evaluation. However, these agents are or will soon be available in bulk, and a significant amount of toxicity information exists that allows a determination of their safety. NFPA has established guidelines to specify agents that can be used in occupied areas. These guidelines specify that the fire suppression or inertion design concentration of agents must be below the cardiac sensitization No Observable Adverse Effect Level (NOAEL) of the agents. NOAEL levels for the Table 3 agents are listed in Table 4 along with the design concentrations for inertion and fire suppression as determined by this work. These minimum design concentrations represent the measured suppression or inertion concentration plus an additional 10% safety factor for inertion and 20% for fire suppression.

From the values in Table 4, only FC-3-1-10 and HFC-23 would be acceptable based on NFPA standards for use in occupied areas designed for protection against propane explosions and fires. HFC-227ea would also be acceptable for use in occupied areas for fire protection only. Of the other agents that are not commercially available in the near-term, CAAs offer the greatest potential for replacing Halon 1301 with equal or better performance. Of the CAAs, the fluoroiodocarbons, in particular the iodinated analog of Halon 1301 (FIC-1311), appear to be the most promising from an effectiveness perspective.

Table 1. *Candidate Fire Suppression Effectiveness Ordered by Storage Volume Equivalents*

Halocarbon No.	MW (g/mole)	Liq. Dens. (g/mL)	Exting. conc. (vol %)	GVEq*	WEq †	SVEq ‡
BFC-21B2	191.81	2.42	1.8	0.62	0.80	0.50
HBFC-123B2	241.81	2.22	1.9	0.66	1.06	0.72
HBFC-123aB2	241.81	2.17	2.0	0.69	1.12	0.78
FIC-13I1	195.91	2.36	3.0	1.03	1.36	0.87
FIC-115-I1	245.91	2.07	2.1	0.72	1.20	0.87
HBFC-124B1	180.92	1.85	2.9	1.00	1.22	0.99
Halon 1301	148.91	1.50	2.9	1.00	1.00	1.00
HBFC-22B1	130.90	1.55	4.4	1.52	1.33	1.29
FIC-217caI1	295.92	2.06	3.0	1.03	2.06	1.50
FIC-217baI1	295.92	2.10	3.2	1.10	2.19	1.57
HFC-32	52.02	0.98	8.8	3.03	1.06	1.62
FIC-319aI1	345.92	2.01	2.8	0.97	2.24	1.67
BTFB §	206.96	1.36	3.5	1.21	1.68	1.85
FIC-5-1-13aI1	445.94	2.05	2.5	0.86	2.58	1.89
HFC-236fa	152.04	1.37	5.6	1.93	1.97	2.16
BCTFB #	233.40	1.68	4.5	1.55	2.43	2.16
HCFC-133a	118.50	1.39	7.6	2.62	2.09	2.25
FC-116	138.01	1.59	7.8	2.69	2.49	2.35
HFC-236ea	152.04	1.42	6.6	2.28	2.32	2.45
HFC-227ea	170.03	1.42	6.3	2.17	2.48	2.62
FC-3-1-10	238.03	1.52	5.0	1.72	2.76	2.72
HFC-227ca	170.03	1.39	6.5	2.24	2.56	2.76
HCFC-124	136.48	1.38	8.2	2.83	2.59	2.82
FC-218	188.02	1.35	6.1	2.10	2.66	2.95
HCFC-22	86.47	1.17	11.6	4.00	2.32	2.98
FC-5-1-14	338.03	1.68	4.4	1.52	3.44	3.08
HFC-134a	102.03	1.20	10.5	3.62	2.48	3.10
FC-6-1-16	388.03	1.73	4.0	1.38	3.59	3.12
FC-14	88.00	1.33	13.8	4.76	2.81	3.17
HFC-245cb	134.05	1.20	8.2	2.83	2.55	3.18
HFC-125	120.02	1.23	9.4	3.24	2.61	3.19
HFC-134	102.03	1.20	11.2	3.86	2.65	3.31
FC-C-318	200.04	1.48	7.2	2.48	3.34	3.38
HFC-23	70.01	0.67	12.6	4.34	2.04	4.57

* GVEq=Gas Volume Equivalent
† WEq=Weight and Equivalent
‡ SVEq=Storage Volume Equivalent
§ 4-Bromo-3,3,4,4-tetrafluoro-1-butene
# 4-Bromo-3-chloro-3,4,4-trifluoro-1-butene

Table 2. ***Explosion Prevention Performance Ordered by Storage Volume Equivalent, Propane As Fuel***

Chemical	MW (g/mole)	LD* (g/mL)	ICst † (vol %)	GVEq ‡	WEq §	SVEq #
Halon 1301	148.91	1.50(30)	4.3	1.00	1.00	1.00
FIC-13I1	195.91	2.36(-42)	5.2	1.21	1.59	1.01
HBFC-124B1	180.92	1.85**	5.8	1.35	1.64	1.33
HFC-152a ††	66.05	0.91	10.1	2.35	1.04	1.72
HBFC-22B1	130.92	1.55	8.8	2.05	1.80	1.74
BTFB ‡‡	206.98	1.357	5.3	1.23	1.71	1.89
FIC-319I1	345.92	2.01(20)	4.9±0.6 §§	1.14 §§	2.65 §§	1.98 §§
HFC-32 ††	52.02	0.98	17.8	4.14	1.45	2.21
HFCs-32/125 ##	67.3	1.07(21)	16.3	3.79	1.71	2.40
FIC-217cal1	295.92	2.06(20)	7.6±0.4 §§	1.77 §§	3.51 §§	2.56 §§
HFC-254cb	116.01	1.0**	9.7	2.26	1.76	2.64**
HFC-236fa	152.04	1.37***	10.5	2.44	2.49	2.73**
HFC-245cb ††	134.05	1.20**	10.7	2.49	2.24	2.80**
HFC-134a	102.03	1.20	14.1	3.28	2.25	2.81
HFC-134	102.03	1.20**	14.5	3.37	2.31	2.89
HCFC-124	136.48	1.38	12.6	2.93	2.69	2.92
HFC-236ea	152.04	1.42**	11.7	2.72	2.78	2.93**
CO_2	44.0	1.03(-20)	29.7	6.91	2.04	2.97
FIC-115I1	245.91	2.07(28)	11.0	2.56	4.22	3.06
N_2	28.01	0.8	38.0	8.84	1.66	3.12
FC-4-1-12	288.03	1.63	7.6	1.77	3.42	3.15
FC-116	138.01	1.59(-73)	15.9	3.70	3.43	3.23
FC-14	88.01	1.33(-80)	21.1	4.91	2.90	3.27
HFC-227ea	170.03	1.42	11.9	2.77	3.16	3.34
HCFC-22	86.47	1.17	19.4	4.51	2.62	3.36
HFC-125	120.02	1.23(20)**	14.7	3.42	2.76	3.36
FC-5-1-14	338.03	1.68	7.2**	1.67**	3.80**	3.39**
FC-6-1-16	388.03	1.73	6.5	1.51	3.94	3.42
FC-3-1-10	238.03	1.52	9.6	2.23	3.57	3.52
FC-218	118.02	1.35	11.2	2.60	3.29	3.65
HFC-227ca	170.03	1.39**	12.9	3.00	3.43	3.70
FC-C-318	200.04	1.48(11)	11.7	2.72	3.66	3.70
HCFC-142b ††	100.5	1.12	19.5	4.53	3.06	4.10
HFC-23	70.01	0.67	19.5	4.53	2.13	4.77

* Liquid density (LD) at 25˚C unless noted in parentheses
† ICst = Stoichiometric inerting concentration
‡ GVEq.= Gas Volume Equivalent
§ WEq = Weight Equivalent
\# SVEq = Storage Volume Equivalent
** Estimate
†† Flammable compound
‡‡ 4-Bromo-3,3,4,4-tetrafluoro-1-butene
§§ Number of tests limited due to small sample amounts. IC is midpoint of concentrations resulting in an explosion (-value) and no explosion (+ value)
\## 60% HFC-32/40% HFC-125
*** Measured.

Table 3. *NFPA Near-Term Halon 1301 (Halocarbon) Replacement Candidates**

Number designation	Chemical name	Chemical formula
FC-3-1-10	Perfluorobutane	C_4F_{10}
HBFC-22B1	Bromodifluoromethane	CHF_2Br
HCFC-124	Chlorotetrafluoroethane	$CHClFCF_3$
HCFC Blend A	Dichlorotrifluoroethane (HCFC-123), 4.75%	$CHCl_2CF_3$
	Chlorodifluoromethane (HCFC-22), 82%	$CHClF_2$
	Chlorotetrafluoroethane (HCFC-124), 9.5%	$CHClFCF_3$
	4-Isopropenyl-1-methyl-1-cyclohexene (d-limonene), 3.75%	C_6H_{10}
HFC-23	Trifluoromethane	CHF_3
HFC-125	Pentafluoroethane	CHF_2CF_3
HFC-227ea	Heptafluoropropane	CF_3CHFCF_3

* NFPA 2001 Standard on Clean Agent Fire Extinguishing Systems, National Fire Protection Association, 1994 Edition.

Table 4. *Cardiotoxicity Values and Inertion Design Concentrations for NFPA Near-Term Agents**

Number Designation	Design concentration † Inertion, Propane (vol %)	Design concentration † Fire Suppression (vol %)	NOAEL ‡ (vol %)	LOAEL § (vol %)
FC-3-1-10	10.6	6.0	40	>40
HBFC-22B1	9.7	5.3	2	3.9
HCFC-124	13.9	9.8	2.5	1.0
HCFC Blend A	19.8	7.2 (13.4) #	10	>10
HFC-23	21.5	15.1	50	>50
HFC-125	16.2	11.3	7.5	10
HFC-227ea	13.1	7.6	9.0	10.5

* NFPA 2001 Standard on Clean Agent Fire Extinguishing Systems, National Fire Protection Association, 1994 Edition.
† Minimum design concentration is determined by the laboratory test plus 10% safety factor for inertion and 20% safety factor for fire suppression. Values from this work.
‡ NOAEL = Highest tested concentration at which no adverse cardiac effects were observed. Adverse cardiac effects generally refer to multiple irregular heart beats, arrhythmia, or death.
§ LOAEL = Lowest tested concentration at which adverse cardiac effects were observed.
\# Manufacturer's design concentration determined by UL Canada as provided in NFPA 2001. Design concentration based on this work given in parentheses.

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The complete report, entitled "Low Ozone-Depleting Halocarbons As Total-Flood Agents: Volume 2—Laboratory-Scale Fire Suppression and Explosion Prevention Testing," (Order No. PB96-109079; Cost: $27.00, subject to change) will be available only from

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